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ABSTRACT

The self-diffusion isotope effect has been determined for Zr^{89} and Zr^{95} diffusing in β zirconium. The migration rate is independent of the tracer mass within experimental error at 942°, 1186°, 1784° and 1815° C. The maximum value of D_{89}/D_{95} is 1.002 ± 0.005.

An anneal at 1750° C for 8 hours immediately followed by the deposition and diffusion of Nb^{95} in the β phase at 1025° C resulted in a three-fold reduction of the diffusion coefficient over that measured conventionally by depositing the tracer at room temperature in the α phase.

It is tentatively suggested that the anomalous diffusion characteristics of Zr, Ti and Hf can be accounted for by the presence of a dense network of short circuit paths introduced into the β phase during the α/β transformation. These defects appear to be relatively stable and can only be reduced in concentration by a prolonged anneal close to the melting temperature.

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INTRODUCTION

Self diffusion in the "normal" b.c.c. metals such as tantalum[1] and molybdenum[2] may be represented by an Arrhenius or thermal activation relation $D_t = D_o e^{-Q/RT}$ which describes the temperature dependence of the diffusion coefficient in terms of a temperature independent energy of activation Q which is related empirically to the melting temperature.[3] The frequency factor D_o takes values from 0.1 to 10 cm^2/sec.[4] and can be adequately described in terms of the thermodynamic and geometric properties of the lattice.

In the anomalous metals titanium,[5] zirconium,[6] and hafnium,[7] an Arrhenius representation gives a temperature dependent value of Q in the β phase which increases from approximately 1.30 eV, just above the c.p.h.-b.c.c. transition, to 3.00 eV at the melting point compared to a Q of 3.00 to 3.50 eV suggested by the melting rule. In the temperature range 800° to 1400° C the frequency factor is at least an order of magnitude smaller than that for a normal metal and is characteristic of dislocation or grain boundary migration rather than volume diffusion.[8]

The author suggested in an earlier paper[9(b)] that two competitive mechanisms could explain the anomalous temperature dependence of diffusion. The approach towards normal values of Q and D_o at high temperature indicated that perhaps a single vacancy exchange mechanism could only effectively dominate the diffusion behaviour at high temperature due to the presence of a low Q mechanism which existed throughout the β phase.

The isotope effect measurement provides a test for this hypothesis. The recent measurement of the isotope effect for self diffusion in b.c.c. iron[10(a)] is consistent with diffusion via single vacancy exchange and is equal to 0.72 within the experimental error. If single vacancy exchange occurs in βZr at high temperature we should observe an isotope effect equal to 0.72. At lower temperatures the appearance of a different value for the isotope effect would provide support for the hypothesis of two competitive mechanisms.

To investigate this possibility the mass dependence of the self-diffusion rate for zirconium has been measured at four temperatures in the β phase. The mass dependence is related to the isotope effect E at a temperature T by the expression[11,12]

$$ E = \left(\frac{D_{89}}{D_{95}} - 1 \right) \bigg/ \left[\left(\frac{m_{89} + (n-1)m_o}{m_{95} + (n-1)m_o} \right)^{-\frac{1}{2}} - 1 \right] \tag{1} $$

where n is the number of ions involved in each diffusion jump, m_{89} and m_{95} are the respective masses of the tracer ions Zr^{89} and Zr^{95} and m_o is the mean mass of the solvent ion. In the self-diffusion isotope effect measurement the tracers are of the same chemical species as the solvent ions, and the correlation factor for diffusion f_c is related to E by the expression[13,14]

$$ E = \Delta K f_c \, (0 < \Delta K \leq 1) \tag{2} $$

where the constant ΔK represents the relation between the "effective" masses of the tracer ions required for the derivation of f_c and the real masses used in the definition of E. In general ΔK is expected

to be close to unity indicating that the diffusing atom possesses most of the translational kinetic energy during its motion across the saddle point of the diffusion barrier. This assumption has been verified experimentally for self diffusion in the metals palladium (f.c.c.)[15] and iron (f.c.c. and b.c.c.).[10]

EXPERIMENTAL TECHNIQUE

Cylinders of 3 pass zone refined zirconium, purchased from the Materials Research Corporation, were annealed at 1200° C for 4 hours, under a vacuum of 10^{-6} torr, in an aluminum oxide tube resistance furnace in the presence of a zirconium foil getter. This produced a stable grain size of 5 to 7 mm. The ends of each cylinder were ground and lightly etched with a 50% H_2O, 47% HNO_3, 3% HF solution. An ammonium oxalate solution containing approximately equal quantities of Zr^{89} and Zr^{95} was placed on one end of each sample and evaporated to dryness. The Zr^{89} and $Zr^{95}-Nb^{95}$ mixture were obtained from the Nuclear Science and Engineering Corporation and an extraction of Zr^{95} was performed immediately prior to the diffusion anneal using a Dowex ion exchange column.[16] The Zr^{95} contained less than 1% Nb^{95} after this procedure. The extraction efficiency was determined by following the subsequent appearance of the γ peak for the daughter Nb^{95} using a solid state detector with a resolution of 2 KeV.

A pair of cylinders, with their diffusion faces separated by a piece of zirconium foil, were wrapped in the same foil and placed inside tantalum cans sealed by electron beam welding under a vacuum of 10^{-5} torr. The diffusion heat treatments at lower temperature were

performed in the furnace already described and the runs at 1784° C

and 1840° C were performed in a tungsten basket furnace. Both fur-

naces maintained a vacuum below 10^{-6} torr during the diffusion anneals.

Temperature was measured to within $\pm 0.1\%$ using either Pt-PtRh or

W-WRe thermocouples in good thermal contact with the tantalum can.

After diffusion had occurred the samples were removed from the

tantalum cans and each was reduced in diameter (to avoid errors in-

troduced by vapor or surface diffusion) and sectioned by lathe or

mircotome.[10(b)] The individual sections were weighed, dissolved in

HCl and placed in thin-walled plastic vials. A 3 in. diameter NaI

"well" scintillation detector with a resolution of 8% was used to

determine the Zr^{89} activity of each section. The γ peak at 0.91

MeV was isolated by a single channel analyzer and sufficient counts

were recorded to give an accuracy of 0.1%.

Figure 2 shows that the γ resolution of the detector was suf-

ficient to exclude any significant level of Zr^{95}-Nb^{95} activity in the

Zr^{89} channel.

Samples were counted in random order and the section having the

highest activity was used at intervals during the count to determine

any changes in the measuring equipment. The dead time of the system

was determined before and after each counting session and correction

was made for lost counts, background and decay during the counting.

The sections were then stored for 10 half lives of the Zr^{89} (33 days)

and counted for their combined Zr^{95}-Nb^{95} activity. Correction for the

decay during counting of the Zr^{95}-Nb^{95} was made by using a decay

coefficient for the mixture at the time of counting. Counting to stand-

ard solutions containing an identical ratio of $Zr^{89}/Zr^{95}\text{-}Nb^{95}$ but having differing total activities showed that measured ratios of $Zr^{89}/Zr^{95}\text{-}Nb^{95}$ were independent of count rate.

At the highest temperatures the quantity of daughter produced in the time interval between purification of the Zr^{95} and the completion of the heat treatment was sufficiently small to make correction for the daughter concentration formed during the anneal unnecessary. At the lowest temperatures, however, a correction based on the calculation in the appendix was applied to the final $Zr^{95}\text{-}Nb^{95}$ count. It is the relative concentration of Zr^{95} plus Zr^{95} which has decayed into Nb^{95} compared to that of Zr^{89} which is required for the isotope effect. Thus the presence of Nb^{95} daughter does not of itself introduce an error into the results. An error arises only from the fraction of Nb^{95} present which diffused as Nb^{95} during the diffusion anneal.

Each section was counted twice for both Zr^{89} and $Zr^{95}\text{-}Nb^{95}$ resulting in four plots of

$$\ln\left(\frac{N_{89}}{N^{*}_{95}}\right) \text{ versus } \left(1 - \frac{D_{89}}{D_{95}}\right)\frac{-x^{2}}{4D_{89}t}$$

where N_{89} is the corrected count for Zr^{89}, N^{*}_{95} represents the count on both Zr^{95} and Nb^{95} and D is the diffusion coefficient for the appropriate tracer isotope. The penetration depth and time for the diffusion anneal are given by x and t respectively. The isotope effect data were also plotted as

$$\ln\left(\frac{N_{89}}{N^*_{95}}\right) \quad \text{versus} \quad \left(1 - \frac{D_{89}}{D_{95}}\right)\ln\left(N_{89}\right)$$

There was no significant difference in the slopes determined by the two methods and the former expression was used in Fig. 4.

CHEMICAL AND RADIO CHEMICAL IMPURITY ANALYSIS

A mass spectrographic analysis of the original material is given in Table I and is compared with that determined after a grain growth and high-temperature diffusion anneal had been performed. This analysis of the original material differs from the manufacturer's batch analysis which suggested an overall purity of 99.99%. No radioactive impurities were determined in either the Zr^{89} or Zr^{95}-Nb^{95} γ spectra recorded by the solid state detector after the preparation of the diffusion samples. The detection efficiency was at least 1% close to the γ peaks and considerably better at other γ energies. Gamma spectra taken from the first few sections after the diffusion heat treatment showed no evidence of slow diffusing impurities but the lower activity of the deeper sections did not permit an exhaustive search for fast diffusing impurities.

THE EXPERIMENTAL RESULTS

The measured diffusion coefficients for Zr^{89} and those of Federer and Lundy[6] for Zr^{95}-Nb^{95} are shown in Fig. 1. The diffusion profiles and isotope effect plots are given in Figs. 3 and 4, respectively. The penetration profiles obey the appropriate theoretical relation, given below, for diffusion from a thin depletable source into a semi-

infinite solid within the experimental error of the data points.

$$C(x,t) = \frac{S_o}{\sqrt{\pi D t}} \exp \left(- \frac{x^2}{4Dt} \right)$$

The initial quantity of tracer is represented by S_o and $C(x,t)$ is the concentration of tracer at point x at time t. The diffusion coefficients calculated from the slopes of the penetration profiles are given in Table II.

The isotope effect plots are straight lines for the measurements at the higher temperatures but at $942°$ C there is an increase in the ratio of Zr^{89}/Zr^{95}-Nb^{95} close to the specimen surface. It is suspected that the oxalate complex on the surface contributed impurities which remained in the diffusion zone throughout the diffusion anneal. The breakdown of this impurity complex liberates oxygen, nitrogen, and hydrogen in quite high local concentrations. However, the very high diffusivities of nitrogen and hydrogen[17] would lead to a rapid reduction in their concentration in a time short compared to the tracer diffusion anneal at all temperatures. For oxygen[17] this is true at high temperatures, however, at $942°$ C the diffusivity of oxygen is a factor 10 slower than that for zirconium self diffusion. Thus a high local concentration $>1.0\%$ could explain the anomally in the isotope effect in a region corresponding to the diffusion zone for oxygen. The relative diffusion rate D_{89}/D_{95} was determined by least squares analysis for all data points at $1120°$, $1784°$ and $1840°$ C for those at greater depths than $4x10^{-5}$ cm^2 at $942°$ C.

From Table III we observe that the isotope effect is less than 0.2 suggesting that the self-diffusion tracers diffuse at a rate which is

effectively independent of their mass. This behavior is not in agreement with the recent work by the author[10(a)] on the self-diffusion isotope effect in b.c.c. iron where the mass dependence of tracers Fe^{55} and Fe^{59} is consistent with diffusion via a single vacancy exchange mechanism giving an isotope effect of 0.7 ± 0.06. Before discussing the isotope effect, the sources of possible measurement errors, which might give rise to such a result, will be reviewed briefly.

The simple decay technique used to determine the activity distribution of the individual tracers does not raise any problems in the interpretation of the experimental results and our discussion will be limited to an examination of the possible presence and influence of impurities during the diffusion anneal.

Examination of the tracer spectra both before and after the diffusion heat treatment, using a solid state detector of 2 KeV resolution, showed no characteristic γ peaks which could be attributed to any impurity other than Nb^{95}. Furthermore, serious contamination by radioactive impurities would be shown by nonlinearity in both the penetration profile and isotope effect plots and it can be seen, from Figs. 3 and 4, with the exceptions of the measurement at 942° C, that this did not occur.

The γ spectrum of Nb^{95} is identical to that of Zr^{95} within the 8% resolution of the NaI counter and the diffusion of a significant quantity of this material during the heat treatment would have increased the measured isotope effect, as Nb^{95} diffuses more slowly than Zr^{95}. In order to minimize the quantity of Nb^{95} present at the beginning of the diffusion anneal a maximum of 1 hour was permitted to elapse

between the purification of the Zr^{95} and the start of the diffusion anneal. The quantity of Nb^{95} produced before and during the diffusion run can be computed from the $Zr^{95}-Nb^{95}$ transformation curve in the appendix (Fig. 6), and it can be shown that correction of the Zr^{95} penetration profile for Nb^{95} is insignificant for the high-temperature runs and reaches a magnitude of only a few percent at the lowest temperatures.

An analysis of nonradioactive impurities present in the zirconium before and after a high-temperature diffusion anneal shows no significant change in the levels of distributed substitutional or interstitial impurities with the singular exception of oxygen which is increased by a factor of 8. Work by Peart[18] on solute diffusion in βtitanium has shown that there is no significant difference in the diffusion properties of iodide titanium as compared to commercial 120 titanium. In the former material individual substitutional impurities are at levels of a few p.p.m. while oxygen is at a level of around 200 p.p.m. For the latter material substitutional impurities, such as iron, reach a level of $2x10^3$ p.p.m.;[19] oxygen is normally 500 p.p.m. and has been doped to levels of 10^4 p.p.m.[19] without any significant change in the measured diffusion coefficient. Unfortunately, the analysis does not evaluate the impurities present in the diffused region during the heat treatment but it is clear from the above work on βtitanium that quite high levels of contamination would not seriously affect the measured diffusion coefficients.

The isotope effect measurement at 942° C in this paper suggests that a high concentration of interstitial oxygen can alter the isotope

ratio where no change in the penetration profile is detectable but the ratio appears to be altered in a highly localized area where the impurity is concentrated. Clearly, when the concentration of oxygen reaches a level where the configuration of the metal lattice is significantly changed the isotope effect will not be representative of the pure zirconium lattice, but it seems justifiable to assume that at or below 1000 p.p.m. oxygen where the pure zirconium lattice is moderately intact the relative diffusion rate of two isotopes differing only in their mass from each other and the lattice atoms, will not be strongly dependent on the presence of oxygen interstitials.

The method of depositing the isotope on the specimen surface was dictated by the necessity for a rapid Zr^{95}, Nb^{95} separation and the minimal loss of time before starting the diffusion anneal. In a diffusion study of Nb^{95} in βzirconium Federer and Lundy[6] used a similar method for depositing the tracer. The author has made measurements on the same system, which are described later in this paper, using a vacuum evaporation technique for depositing the tracer and has found no significant difference in the diffusivities measured by the two methods. The presence of barriers to diffusion at the surface might be expected in solute diffusion experiments but such problems do not appear to arise in the presence of the oxalate complex and are even less significant in self-diffusion experiments where isotopic exchange would guarantee unimpeded entry of the tracer into the host lattice.

From these considerations it is concluded that the results obtained for the isotope effect are not artifacts of the experimental method but represent the real mass dependence of self-diffusion tracers in

this system.

DISCUSSION

A small value for the isotope effect has been observed for iron
diffusing in βTi.[20] This result is more difficult to interpret than
the self-diffusion measurement but it seems reasonably certain that
the major mechanism of diffusion in these metals is not simple vacancy
exchange. The two mechanism hypothesis has not been justified by the
results though it could be argued that the metal melts before normal
vacancy exchange can successfully compete with the low temperature
migration process.

Some years ago an experiment was performed by Kidson and McGurn[21]
in which zirconium diffusion samples were annealed for up to 1 hour
at 1200° C followed by deposition of a tracer without lowering the
sample temperature through the α/β phase transition. The diffusion
rates obtained by the above method were found to be no different from
those determined by a conventional experiment and it was assumed that
any defects introduced at the phase change must anneal out in a time
which is small compared to the length of a typical diffusion anneal.

In view of the unusual result for the isotope effect which might
indicate diffusion via short circuit paths such as dislocations the
Kidson and McGurn experiment was repeated using a much higher annealing
temperature.

Two samples of Zr were prepared for deposition of the tracer iso-
tope Nb^{95} but were first raised to a temperature of 1750° C for 8
hours in an induction furnace under a vacuum of 10^{-6} torr. The tempera-

ture was then reduced to $1025^{\circ}\pm20^{\circ}$ C and held constant within $\pm5^{\circ}$ C.
One specimen was then lowered from the induction coil and cooled to
750° C (120° C below the transformation temperature). After 30
minutes at this temperature the specimen was raised to its original
position in the heater coil and the end surfaces of both specimens
were covered by thin evaporated deposits of Nb^{95}. The specimens were
heated for a further 4 hours and then sectioned by microtome. The
diffusion coefficients measured from the penetration profiles differed
by a factor of 3. The penetration profiles for these two samples are
shown in Fig. 5. The higher coefficient was determined from the speci-
men which had been passed through the α/β phase transition immediately
before the diffusion heat treatment. Zr^{89} was temporarily unavailable
at the time the experiments were performed and the solute tracer most
closely resembling the solvent lattice ion was used.

The host material was of a lower level of purity than that used
for the isotope effect experiment but as enclosure in tantalum cans was
not possible there seemed to be no significant advantage in the use of
triple zone refined material. Both diffusion samples had almost iden-
tical thermal histories and it would be unreasonable to attempt to
explain the difference in diffusion properties in terms of differing
levels of impurities in the two samples.

It is concluded from this experiment that the α/β transition in
zirconium produces some form of short circuit path or complex which is
capable of enhancing the solute diffusion rate and can only be removed
by relatively long anneals at temperatures close to the melting point.
It should be noted that the time required at high temperature is long

compared to the length of a typical diffusion anneal at these temperatures.

It is clear that a full understanding of the isotope effect results must await a detailed ecamination of this new short circuit phenomenon in zirconium. However, it is appropriate to mention some supporting evidence for the presence of a high dislocation density in the β phase of zirconium extending to much higher temperatures than has been proposed on the basis of the observation of time dependent diffusion coefficients for impurity diffusion in β titanium close to the α/β transformation reported by Gregory and Askill.[22]

The suggestion that short circuit paths, dislocations for example, might be responsible for the unusual diffusion behavior of the anomalous b.c.c. metals is not new but there has been considerable difficulty in accepting the large estimates of the dislocation density required to explain the observed diffusion coefficients. The absence of detectable grain boundary diffusion by autoradiographs even at the lowest temperatures in the β phase of titanium[18] suggests that the rate of migration along grain boundaries and, by implication, also along dislocations does not differ greatly from that through the crystal volume. Thus, in order to explain observed diffusion rates at low temperature entirely in terms of dislocation diffusion, it is necessary to postulate dislocation densities in the range 10^9 to $10^{11}/cm^2$.[9]

To the author's knowledge there are no direct determinations of dislocation density in the β phase of either titanium or zirconium and the only alternative is to examine some of the properties of these metals in order to see if any circumstantial evidence exists for a high density of dislocations.

The metals zirconium and titanium both undergo self deformation at high temperatures. This appears to involve a gross movement of single crystal regions with respect to one another. This phenomenon has only been observed at temperatures above 1600° C and has often led to rejection of diffusion samples as it has been impossible to section parallel to the original interface because of the relatively small surface area of the disorientated single crystals. This massive movement of large regions with respect to one another could readily absorb large numbers of dislocations and lead to a significant decrease in the dislocation density. This behavior could be explained by postulating large dislocation densities immediately after the α/β transformation which are stable until a relatively high temperature is reached.

Only one electron microscope examination of zirconium is known to the author. This work on αzirconium by Howe, Whitton and McGurn[23] suggests that densities of the order of $2 \times 10^9/\text{cm}^2$ are typical of this material but it is necessary to show that this dislocation density remains unchanged by passage through the phase transformation.

Glen and Pugh[24] showed that for a transition from $\alpha \to \beta \to \alpha$ a single crystal of αzirconium might be expected to transform into one of 57 different α orientations. Laue photographs show that such a series of transformations invariably reproduce the original α orientation. They suggested that dislocations and stacking faults were probably responsible for the "memory" associated with the diffusionless shear transformation observed in this metal.

The β dislocation densities appear to be stable in the transformation

and high densities of dislocations may be transferred from on phase to the other. There is clearly a necessity for further experimental evidence before short circuit paths can be considered an explanation of the diffusion anomaly in β zirconium. It is unlikely that it will be possible to obtain electron microscope transmission pictures of dislocations in the β phase but work is at present being undertaken on a detailed investigation of the structure of the α and β phases of zirconium using X-ray techniques.[25] An experimental examination of the influence of high temperature anneals on self diffusion is also under way at the NASA-Lewis Research Center. It is hoped that an investigation of the kinetics of high-temperature annealing will make it possible to determine the real self-diffusion temperature dependence in the absence of large concentrations of short circuit defects.

The isotope effect for diffusion in a dislocation matrix of the kind suggested is difficult to estimate. If the problem is considered as diffusion along an idealized edge dislocation, which might be the case for the strong segregation of an impurity tracer, then we should expect an isotope effect corresponding to the inverse square root of the mass. This, however, seems to be an unrealistic assumption as it does not consider the disorder existing in a real dislocation and it might be expected that the opportunity for relaxation close to the dislocation core would allow considerable kinetic energy transfer between the diffusing ions and those ions forming the diffusion saddle. This could give a value of $\Delta K < 1$. Alternatively, considerable cooperative motion of ions may occur during each diffusion exchange, leading to a dilution of the mass dependence of the tracer ions. At

least seven additional ions would be required to account for the observed isotope effect. Either factor or a combination of both could provide an explanation for the small isotope effect.

SUMMARY

The isotope effect has been determined for Zr^{89} and Zr^{95} diffusing in β zirconium. At the temperatures 942°, 1186°, 1784° and 1815° C the isotope effect was determined to be less than 0.2. An annealing experiment to determine the importance of the diffusionless shear transformation in contributing diffusion short circuit paths to the β phase of zirconium has indicated that a three-fold reduction in the measured diffusion coefficient at 1025° C can be achieved by a heat treatment of several hours close to the melting temperature.

The unusual Arrhenius relation for zirconium, titanium and hafnium and the small isotope effect are tentatively attributed to diffusion on a short circuit network.

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APPENDIX

The kinetics of parent-daughter decay are given by the expressions

$$N_p = N_o e^{-\lambda_p t}$$

$$N_d = \frac{\lambda_p}{\lambda_d - \lambda_p} N_o \left(e^{-\lambda_p t} - e^{-\lambda_d t} \right)$$

where N_o is the initial disintegration rate for the pure parent iso-
tope at time $t = o$, N_p is the disintegration rate for the parent at
time t and N_d is that for the daughter. The symbol λ is used to
denote the decay constant associated with either the parent (λ_p) or
the daughter (λ_d). Figure 6 shows the time dependence of the count
rates for Zr^{95} and Nb^{95}. It is clear that at 1784° and 1815° C, where
the diffusion coefficients for Nb^{95} and Zr^{95} are approximately equal,
that the heat treatments were completed in such a short time that no
significant correction to the $Zr^{95} - Nb^{95}$ count is required for Nb^{95}
formed prior to or during the diffusion anneal.

In order to calculate the influence of daughter diffusion during
the longer heat treatments required at 942° and 1186° C, an equation
for the penetration profile of the combined parent daughter combination
is derived as follows. Consider a one-dimensional diffusion geometry
where $n_p(x,t)$ and $n_d(x,t)$ are, respectively, the volume concentra-
tions of the parent (the tracer) and the daughter decay product as a
function of the distance, x, and the time, t, where x is measured
from the surface of a semi-infinite sample. The dependent variables
will then be independent of y and z.

Let the parent have a decay constant λ_p and a diffusion coefficient D_p. Similarly, the daughter has a decay constant λ_d and a diffusion coefficient D_d. The concentration of the parent is then a solution to the equation

$$\frac{\partial n_p(x,t)}{\partial t} = D_p \frac{\partial^2 n_p(x,t)}{\partial x^2} - \lambda_p n_p(x,t) \qquad (1)$$

This is the usual one-dimensional diffusion equation except for the last term which takes into account the rate of decay of the parent. If the parent has an initial uniform concentration n_{po} in a region of thickness a at the surface of the sample, the boundary conditions are

$$n_p(x,0) = n_{po} \qquad 0 \leqslant x \leqslant a$$

$$= 0 \qquad x > a$$

$$\frac{\partial n_p(0,t)}{\partial x} = 0 \qquad \text{and} \lim_{x \to \infty} n_p(x,t) = 0$$

$$(2)$$

Similarly, the differential equation for the concentration of the daughter is

$$\frac{\partial n_d(x,t)}{\partial t} = D_d \frac{\partial^2 n_d(x,t)}{\partial x^2} + \lambda_p n_p(x,t) - \lambda_d n_d(x,t), \qquad (3)$$

and the boundary conditions are

$$n_d(x,0) = n_{do} \qquad 0 \leqslant x \leqslant a$$

$$= 0 \qquad x > a$$

$$\frac{\partial n_d(0,t)}{\partial x} = 0 \qquad \text{and} \lim_{x \to \infty} n_d(x,t) = 0$$

$$(4)$$

where n_{do} is the initial uniform concentration of the daughter in the thickness a at the surface.

If the thickness, a, of the initial radioactive plating is small compared to the penetration depth, the solutions to these equations are

$$n_p(x,t) = \frac{N_p e^{-\left(\lambda_p t + \frac{x^2}{4D_p t}\right)}}{\sqrt{\pi t D_p}} \qquad (5)$$

and

$$n_d(x,t) = \frac{N_d e^{-\left(\lambda_d t + \frac{x^2}{4D_d t}\right)}}{\sqrt{\pi t D_d}} + \frac{\lambda_p N_p e^{-\left(\frac{\lambda_p D_d - \lambda_d D_p}{D_d - D_p} t\right)}}{D_d - D_p}$$

$$\cdot \int_0^t \left\{ \left(\frac{D_d}{\pi \tau}\right)^{\frac{1}{2}} e^{\left[\frac{D_d(\lambda_p - \lambda_d)\tau}{D_d - D_p} - \frac{x^2}{4\tau D_d}\right]} - \left(\frac{D_p}{\pi \tau}\right)^{\frac{1}{2}} \right.$$

$$\left. e^{\left[\frac{D_p(\lambda_p - \lambda_d)\tau}{D_d - D_p} - \frac{x^2}{4\tau D_p}\right]} \right\} d\tau \qquad (6)$$

where N_p and N_d are, respectively, the initial surface concentrations of the parent and daughter and are related to the initial volume concentrations by

$$N_p = n_{po} a, \lim a \to o \qquad \text{and} \quad N_d = n_{do} a, \lim a \to o \qquad (9)$$

The total counting rate, r_{pd} of a thin section of thickness $\Delta\ell$ and area A including both parent and daughter decays is

$$r_{pd} = \eta \, A\Delta\ell \left[f_p \lambda_p n_p(x,t) + f_d \lambda_d n_d(x,t) \right] \tag{10}$$

where η represents the efficiency of the counter for counting the gammas and f_p and f_d are the respective fractions of the decays of the parent and daughter which result in the measured gamma rays.

As an example the concentration $n_d(x,t)$ was calculated for λ_d equal to 1×10^{-7} reciprocal seconds, and t equal to 2×10^4 seconds for several values of D_p and D_d.

Figure 9 is a plot of the log of $r_{pd}/A \, \Delta\ell \, \eta$ as a function of x^2/t, and shows these results. The short-dashed curves in these fig- ures represent the usual diffusion profile obtained from the counting rate of the parent only. Each of the other curves then represents the diffusion profile obtained by summing the counting rates of the parent and daughter. The curve for $D_p = 1\times10^{-9}$ cm^2/sec and $D_d = 8\times10^{10}$ cm^2/sec represents the measured penetration profile for $Zr^{95} - Nb^{95}$ diffused into zirconium at 942° C for 4 hours.

Figure 9(a), where $D_p > D_d$, shows clearly that the slopes de- rived from the solid curves and hence the apparent diffusion coefficients are only a few percent smaller than the true value given by the re-

ciprocal slope of the dashed line representing the parent alone. However, the influence of the daughter is much more marked in Fig. 9(b) where $D_d > D_p$. In the worst case presented, a diffusion coefficients calculated from a straight line drawn through curves with D_d/D_p of 10 or 100 could overestimate D_p by 25 percent.

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TABLE I

[Results of analysis are expressed as ppm by weight.
Other elements when present did not exceed 5 ppm.]

Element	Isotope effect material		High temperature anneal experiment material
	Analysis of original material	Analysis after grain growth and diffusion[a]	Analysis of original material
C	35	120	97
N	130	36	66
O	140	1100	722
F	15	27	-----
S	40	65	-----
Cl	30	25	-----
Cr	66	39	10
Fe	460	350	180
Ni	4	8	-----
Al	51	44	10
Hf	37	52	100
Ta	2	4	-----

[a]This specimen was given a grain growth heat treatment at 1200° C for 4 hours under a dynamic vacuum of 10^{-6} torr followed by a diffusion heat treatment for 1 hour at 1784° C in a tantalum can sealed under a vacuum of 10^{-5} torr.

TABLE II. - DIFFUSION COEFFICIENTS FOR β ZIRCONIUM

Tracer	Temperature, °C	Time, sec.	Diffusion coefficient, cm^2/sec
Zr^{89}	942±1	1.092×10^4	9.88×10^{-10} 9.23
Zr^{89}	1186±1	1.656×10^4	5.25×10^{-9} 5.45
Zr^{89}	1784±2	3.630×10^3	2.08×10^{-7} 2.21
Zr^{89}	1815±2	3.510×10^3	2.45×10^{-7} 2.48
Nb^{95}	1025±20	1.346×10^4	[a]7.12×10^{-10} [b]2.03

[a] Annealed at 1750° C for 8 hours and diffused after 30 minutes at 750° C in the α phase.

[b] Annealed at 1750° C for 8 hours and diffused without entering the α phase.

TABLE III. - SELF-DIFFUSION ISOTOPE FOR β ZIRCONIUM

Temperature,	Values of $\left(\dfrac{D_{89}}{D_{95}} - 1\right)$ for each sample	Mean value of $\left(\dfrac{D_{89}}{D_{95}} - 1\right)$	E^a
942	- 0.002, - 0.006, + 0.000, - 0.003 - .001, + .001, - .002, + .002	- 0.001±0.003	- 0.03±0.07
1186	+ 0.000, - 0.002, + 0.001, + 0.000 + .001, + .001, + .000, - .001	+ 0.000±0.001	+ 0.00±0.03
1784	+ 0.001, + 0.010, + 0.002, + 0.000 + .000, + .005, + .001, + .000	+ 0.002±0.005	+ 0.06±0.14
1815	+ 0.000, - 0.001, - 0.001, - 0.001 + .002, - .001, - .001, - .001	+ 0.000±0.002	+ 0.00±0.06

^{a}E is determined by assuming n = 1.

log D

$10^4/T, °K$

T, °C

Figure 1

0.511
0.726
0.760
0.906
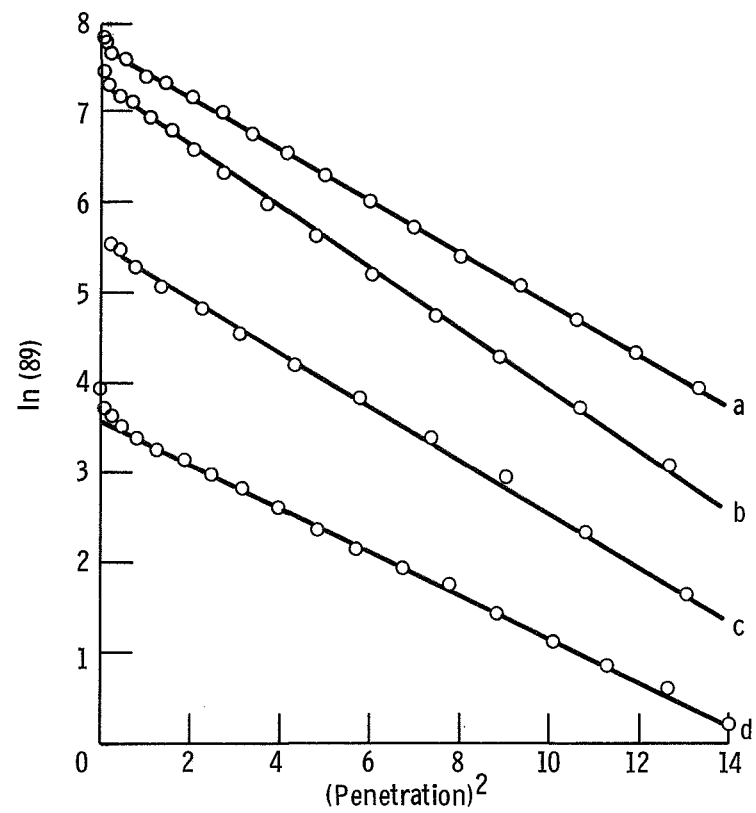
Counts per minute

Energy, MeV
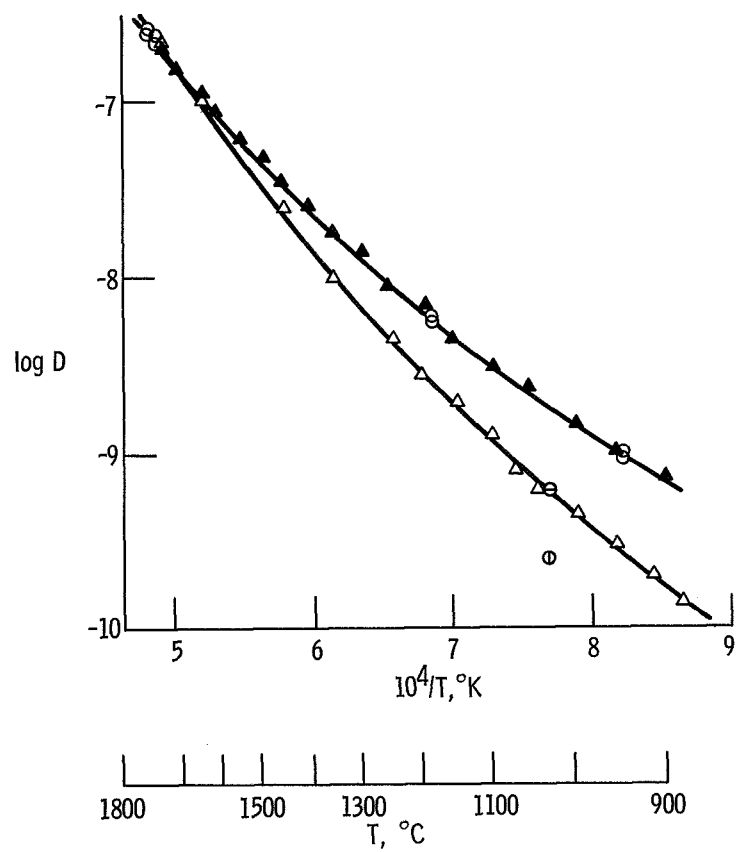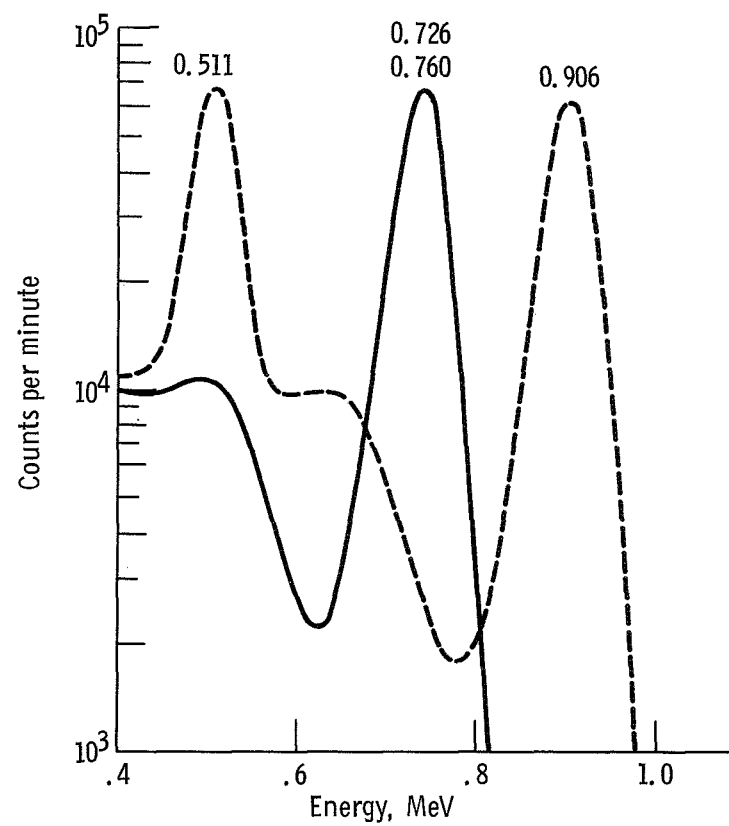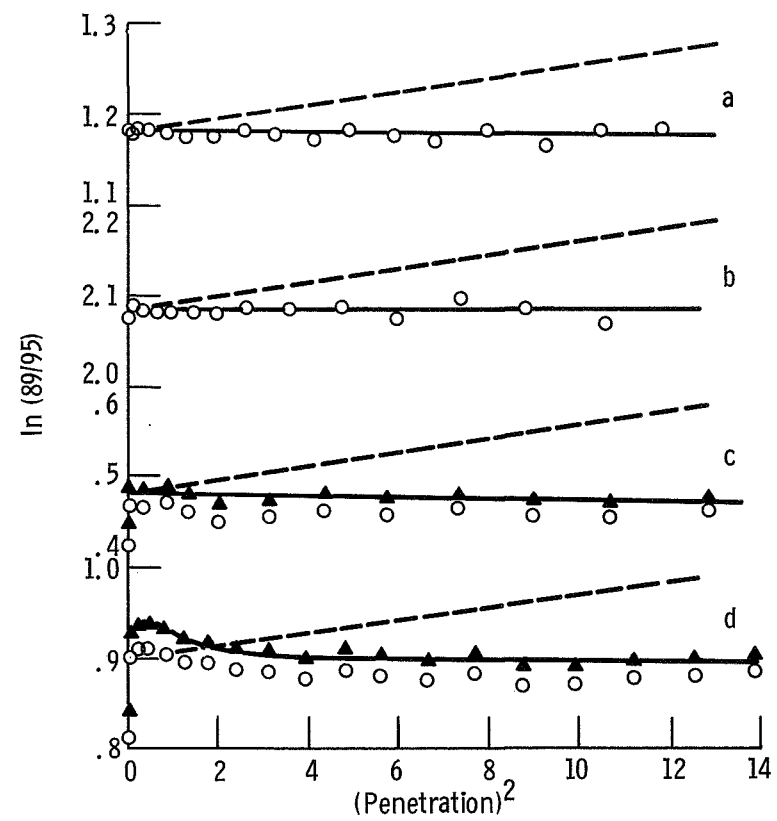
Figure 2

Figure 3

Figure 4
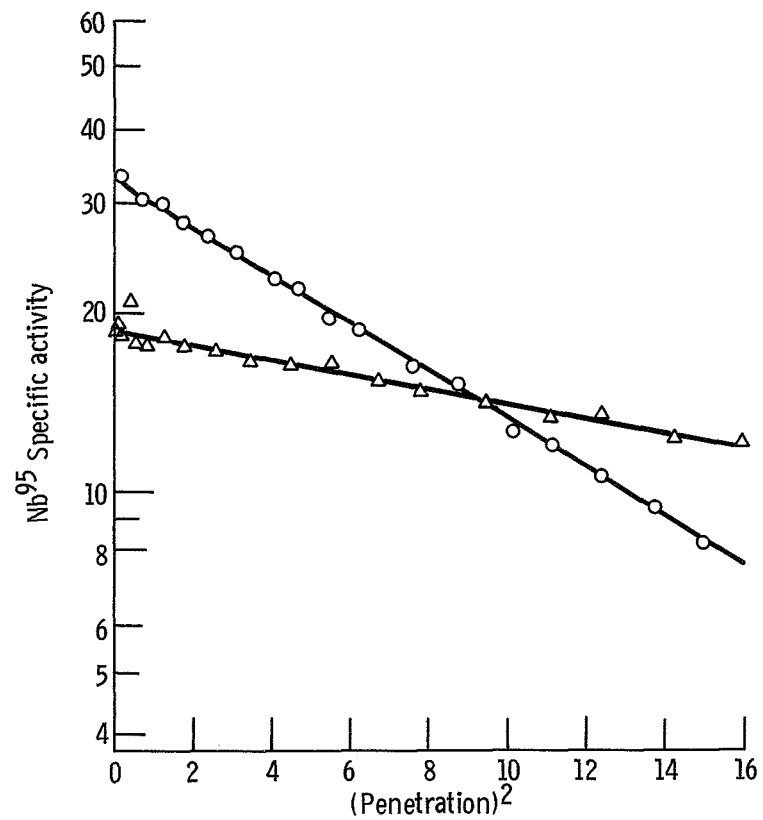
Figure 5. - Scale in units of 10^{-6} cm^2.

Figure 6

(a) Daughter diffusion coefficient less than parent diffusion coefficient.

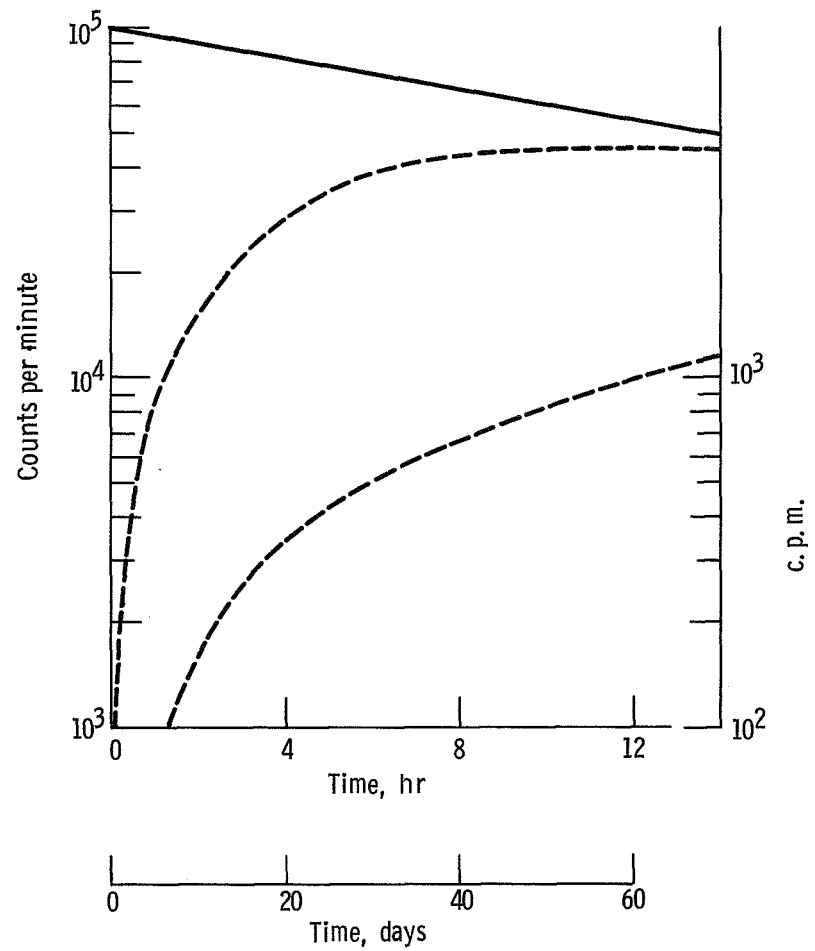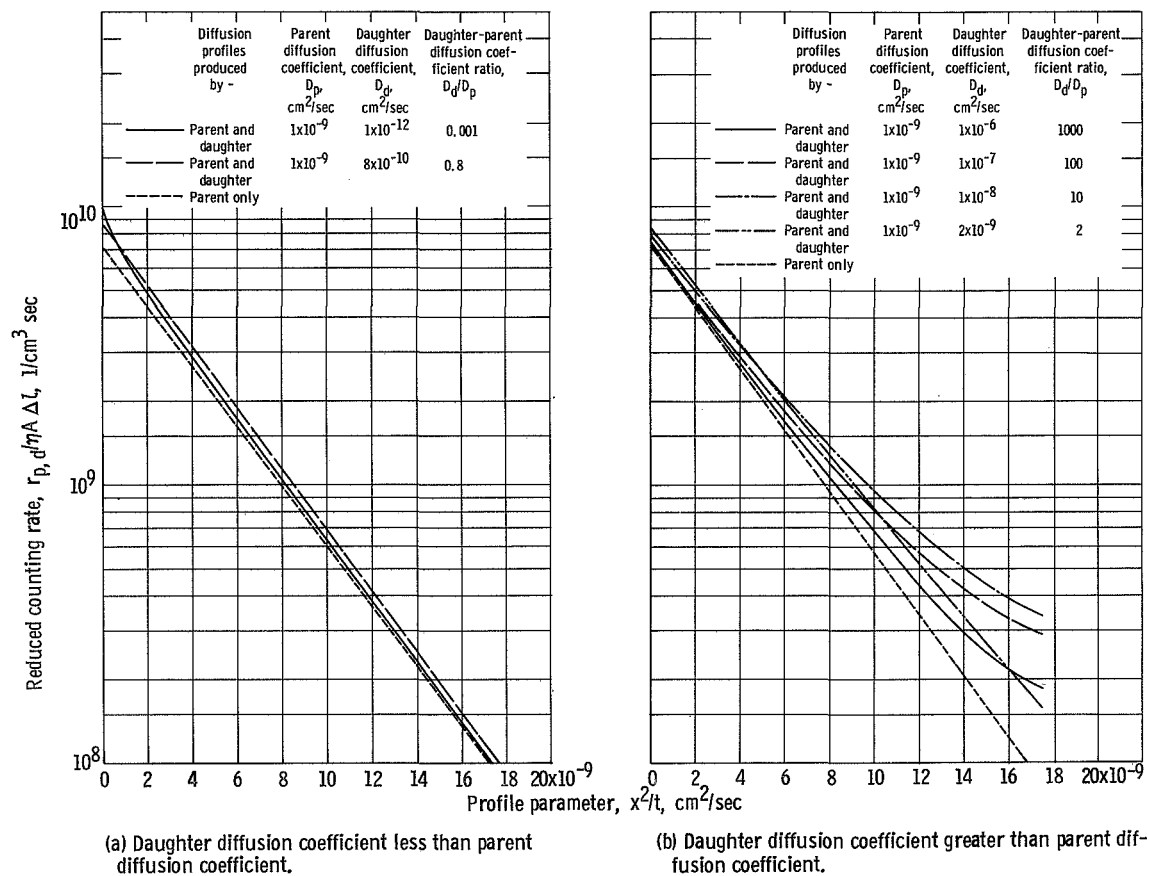(b) Daughter diffusion coefficient greater than parent diffusion coefficient.

Figure 7. - Reduced counting rate as function of diffusion profile parameter.